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Sir:

Transmitted herewith for filing is the patent
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Inventor: Eduardo J. Baralt, et al.

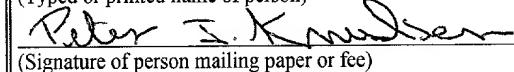
For: OLIGOMERIZATION OF ALPHA-
OLEFINS IN THE PRESENCE OF
CARBOXYLIC ACIDS

Case Docket No. T-5858
Chevron Corporation
Law Department – Patent and Licensing Unit
P. O. Box 6006
San Ramon, CA 94583-0806

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Enclosed are:

- Specification [Total Pages = 12]
- An Assignment of the invention to CHEVRON U.S.A. INC., San Francisco, California, a corporation of the State of Pennsylvania.
- Preliminary Amendment
- Drawing(s) [Total Sheets = 0]
- Combined Oath or Declaration and Power of Attorney [Total Pages = 1]
 - Newly executed (original or copy)
 - Copy from a prior application (37 CFR §1.63(d)) (for continuation/divisional)
 - DELETION OF INVENTOR(S)
Signed statement attached deleting inventor(s) named in the prior application, see 37 CFR 1.63(d)(2) and 1.33(b).
- Incorporation by Reference (*useable if copy of Oath or Declaration from prior application is being submitted*)
The entire disclosure of the prior application, from which a copy of the oath or declaration is being supplied, is considered as being part of the disclosure of the accompanying application and is hereby incorporated by reference therein.
- Information Disclosure Statement.
- If a CONTINUING APPLICATION, *check appropriate box and supply the requisite information:*
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(Col. 1) (Col. 2)

For	No. Filed	No. Extra
Basic Application Fee		
Total claims	9 - 20	0
Independent claims	2 - 3	0
<input type="checkbox"/> Multiple dependent claims presented		

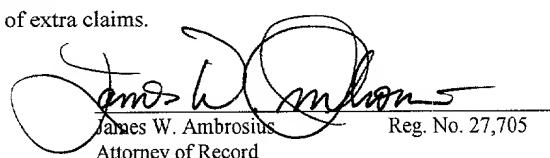
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J. W. Ambrosius
Enclosures

October 2, 2000


James W. Ambrosius
Attorney of Record
P.O. Box 6006, San Ramon, CA 94583-0806
Area Code (925) 973-4503

A
JC675 U.S. PTO
09/1678413
10/02/00

Be it known, that we, EDUARDO J. BARALT, a citizen of Venezuela, resident of Kingwood, Texas, and RUSSELL BAK, a citizen of the United States, resident of the Woodlands, Texas have invented new and useful improvements in

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**OLIGOMERIZATION OF ALPHA-OLEFINS IN THE PRESENCE OF
CARBOXYLIC ACIDS**

RECORDED BY AUTOMATIC RECORDING SYSTEM

OLIGOMERIZATION OF ALPHA OLEFINS IN THE PRESENCE OF CARBOXYLIC ACIDS

FIELD OF THE INVENTION

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The present invention relates to a process for the oligomerization of alpha olefins in the presence of a boron trifluoride/alcohol catalyst with a carboxylic acid used as a modifier to increase the amount of trimer and tetramer in the product.

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BACKGROUND OF THE INVENTION

The oligomerization of alpha olefins in the presence of a Lewis acid catalyst has been used commercially to produce synthetic fluids which are useful for various commercial applications, such as in synthetic lubrication oils, drilling fluids, hydraulic fluids, and heat transfer fluids. The catalyst of choice is usually boron trifluoride combined with a protic promoter, such as butanol or water. See, for example US Patents 4,956,512 and 5,945,574. US Patent 3,769,363 describes the use of an oligomerization catalyst containing boron trifluoride with a carboxylic acid having more than three carbon atoms in the molecule as the promoter. In order to control the degree of oligomerization and increase the amount of trimer in the product, US Patent 3,997,621 teaches the use of an ester in the reaction mixture as a modifier. By controlling the degree of oligomerization the resulting product will have a narrower range of carbon atoms in the molecule which results in more controlled volatility and temperature viscometrics. Generally speaking, it is desirable to produce a product having low volatility and low viscosity for use in crankcase oils.

30 Surprisingly, it has been found that carboxylic acids may be used as a modifier in the oligomerization reaction of alpha olefins to increase the yields

of trimer and tetramer in the product when used in combination with a boron trifluoride/alcohol catalyst complex.

SUMMARY OF THE INVENTION

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The present invention is directed to an improved process for controlling the oligomerization of an alpha olefin in the presence of a catalyst complex comprising boron trifluoride and an alcohol to form a polyalphaolefin product, the improvement comprising including with the catalyst complex in the 10 reaction zone containing the catalyst complex and the alpha olefin a sufficient amount of a carboxylic acid modifier to significantly increase the amount of trimer and tetramer present in the polyalphaolefin product formed as compared to an oligomerization process in which the carboxylic acid is not present, wherein the carboxylic acid contains from 2 to about 10 carbon 15 atoms. The alpha olefin monomer may contain anywhere from 3 to about 22 carbon atoms in the molecule but will preferably contain from 3 to about 14 carbon atoms in the molecule. The oligomerization reaction will proceed over a broad temperature range but is usually carried out in the temperature range of from about 30°C to about 150°C and most preferably within the temperature 20 range of from about 40°C to about 60°C. Following oligomerization the product may be left unsaturated or it may be hydrogenated to saturate the double bonds remaining in the molecule depending on the application for which the product is to be used.

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DETAILED DESCRIPTION OF THE INVENTION

The carboxylic acid used as a modifier according to the present invention should contain from 2 to about 10 carbon atoms in the molecule. The carboxylic acid may contain unsaturated carbon to carbon bonds and the 30 carbon chain may be either branched or unbranched. Examples of suitable modifiers include, but are not necessarily limited to, acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, enanthic acid, caprylic acid,

pelargonic acid, and capric acid. Particularly preferred for carrying out the invention is acetic acid.

The amount of carboxylic acid present in the oligomerization mixture should
5 be at least a sufficient amount to significantly increase the yield of trimer and
tetramer in the final product as compared to an oligomerization mixture which
does not contain the carboxylic acid. In general, a significant increase should
be at least a 20 weight percent increase in the amount of trimer and tetramer
in the product as compared to the oligomerization reaction without the
10 modifier present. The precise amount of carboxylic acid modifier required to
practice the invention will vary somewhat depending upon the carboxylic acid
chosen, the alpha olefin, the temperature of the reaction mixture, the amount
of catalyst, and the ratio of the boron trifluoride to the alcohol promoter.
However, these variables merely require the optimization of the conditions of
15 the oligomerization reaction and, as such, should not require any more than
routine experimentation which is well within the ability of one skilled in the art.

In general, the amount of carboxylic acid modifier will usually be present
within the range of from about 0.08 mole % to about 2.0 mole % of modifier to
20 olefin with about from 0.16 mole % to about 0.35 mole % of modifier being
preferred.

The alpha olefin used as the feed for the oligomerization reaction will usually
contain from 3 to about 22 carbon atoms in the molecule and preferably will
25 contain from 3 to about 14 carbon atoms in the molecule. The alpha olefin, of
course, will contain an unsaturated carbon to carbon bond in the 1-position,
however, the molecule may also contain other internal unsaturated carbon to
carbon bonds in the molecule. In addition , the alpha olefin may be either
branched or unbranched. However, in most instances when practicing the
30 invention the alpha olefins will be mono-olefinically unsaturated, that is, they
will contain only a single double bond in the 1-position, and will be
unbranched, that is, the feed will be comprised of a normal alpha olefin. The

present invention is most advantageous when the alpha olefin feed is a relatively pure alpha olefin, that is, the feed consists primarily of one alpha olefin as opposed to a mixture of different alpha olefins. Examples of alpha olefins which are suitable for use as feeds in practicing the present invention include propene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-decene, 1-dodecene, or 1-teradecene.

The alcohol promoter will be an alcohol having from 1 to about 24 carbon atoms in the molecule, more typically having 12 carbon atoms or less in the molecule. Operable protic promoters include, but are not limited to, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-hexanol, and the like. Particularly preferred as a protic promoters are 1-propanol and 1-butanol.

The amount of boron trifluoride used in the reaction mixture is usually in molar excess relative to the amount of the alcohol promoter. The reaction vessel is typically pressurized with boron trifluoride or a mixture of boron trifluoride and nitrogen. The boron trifluoride may be bubbled through the reaction mixture, introduced as part of the catalyst complex, or otherwise introduced into the reaction mixture, as for example, by mechanical stirring.

Although the oligomerization reaction will proceed over a wide temperature range, the reaction preferably is carried out at a temperature in excess of 30°C, and preferably is carried out at a temperature in excess of 40°C. The upper temperature limit is about 150°C, but as a practical matter the oligomerization reaction mixture is usually maintained at a temperature of less than about 60°C.

The following example is used to further illustrate the invention, but it is not intended to a limitation thereon.

EXAMPLE 1

The reactor was sealed and purged with nitrogen. A reaction mixture consisting of 1000 grams of 1-hexane, 0.35 weight percent 1-propanol, and 5 0.5 weight percent of acetic acid was added to the reactor vessel at a rate of 600 grams per hour. Boron trifluoride was added to the reactor vessel and used to maintain a pressure in the reactor of 30 psi. The reaction mixture was maintained at a temperature of 40 degrees C. After one hour the reaction 10 mixture was washed with caustic water to remove the catalyst. The product was analyzed by gas chromatography. The yield distribution of the product is 10 shown in Table 1 below

EXAMPLE 2

15 The procedure of Example 1 was carried out again except without the acetic acid being present. The results of the experiment are shown in Table 1 below.

EXAMPLE 3

20 The procedure of Example 2 was repeated a second time. The results are shown in Table 1.

TABLE 1

	Example 1	Example 2	Example 3
C6 Monomer	9.65 wt. %	23.53 wt. %	10.60 wt. %
C12 Olefins	2.45 wt. %	1.92 wt. %	0.24 wt. %
C18 Olefins	44.86 wt. %	21.60 wt. %	6.18 wt. %
C24 Olefins	31.19 wt. %	21.35 wt. %	18.12 wt. %
C30 Olefins	8.63 wt. %	15.86 wt. %	27.96 wt. %
C36 Olefins	3.09 wt. %	8.50 wt. %	18.52 wt. %
C42 Olefins	0.13 wt. %	7.82 wt. %	18.38 wt. %

By comparing the yield distribution of products between the three examples, it
5 will be clearly seen that the use of acetic acid as a modifier in Example 1
significantly increased the yield of trimer and tetramer as compared to the
controls in Examples 2 and 3 in which no modifier was present.

EXAMPLE 4

10 The process as described above was repeated using 1-butene as the alpha
olefin and propionic, octanoic (caprylic) and decanoic (capric) acid,
respectively, as the carboxylic acid modifier. The results of each of the
demonstrations was compared to that for acetic acid modifier and are shown
15 in Table 2 below. It should be noted that the amount of trimer present in the
product distribution showed a slight increase with the higher carboxylic acids
as compared to acetic acid. However, the amount of tetramer and higher
oligomers formed were slightly lower when compared with acetic acid.

TABLE 2

Reference	A	B	C	D	E
1-Octene, gr.	27.4	25.5	26.9	24.5	25
1-Propanol gr. acid	2.3	2.3	2.6	2.6	2.3
Acid	Acetic	Acetic	Propionic	Octanoic	Decanoic
Acid, gr.	4.8	4.4	5.8	10.7	12.8
1-Butene, gr.	453.59	444.52	453.59	449.06	453.59
wt.% acid to Butene	1.06	0.99	1.28	2.38	2.82
Mole % acid to Butene	0.99	0.92	0.97	0.93	0.92
BF ₃ consumed, gr.	26.31	25.75	24.47	20.02	27.5 (approx.)
Reaction time	60 min	60 min	60 min	60 min	60 min
Set Temp., °C	20	40	30	45	40
Product Distribution, %					
C8	0.11	0.08	0.06	0.05	0.02
C12	8.04	8.56	13.09	13.58	19.65
C16	23.56	23.80	31.75	24.62	20.46
C20+	68.29	67.56	55.10	61.75	59.88

EXAMPLE 5

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The process as generally described above was repeated using varying amounts of acetic acid. The reaction was allowed to continue for 60 minutes while controlling the temperature at 30°C. The amounts of the modifier and results are shown in Table 3 below.

TABLE 3

Reference	A	B	C	D	E	F	G
Acetic Acid, g	0	0.9	1.0	5.0	8.9	11.3	23.1
1-Butene, g	453.5 9	449.06	453.59	453.59	453.59	449.06	449.0 6
Wt.% Acetic Acid: Butene	0	0.2	0.22	1.10	1.96	2.52	5.15
BF ₃ Consumed	17.08	15.07	18.69	26.72	30.16	36.41	51.57
% of C16 in Product	24.44	31.52	36.89	32.57	28.35	27.00	28.61

- It will be noted that amount of tetramer in the product increased with an increase in the amount of acetic acid present up to 0.22 wt.% (0.19 mole %) of acetic acid to 1-butene and then began to decrease.

What is claimed is:

1. An improved process for controlling the oligomerization of an alpha olefin in the presence of a catalyst complex comprising boron trifluoride and an alcohol to form a polyalphaolefin product, the improvement comprising including with the catalyst complex in the reaction zone containing the catalyst complex and the alpha olefin a sufficient amount of a carboxylic acid modifier to significantly increase the amount of trimer and tetramer present in the polyalphaolefin product formed as compared to an oligomerization process in which the carboxylic acid is not present, wherein the carboxylic acid contains from 2 to about 10 carbon atoms.
2. The process of claim 1 wherein the carboxylic acid modifier is acetic acid.
3. The process of claim 1 wherein the acetic acid modifier is present in an amount of from about 0.08 mole percent to about 2.0 mole percent modifier to alpha olefin.
4. The process of claim 3 wherein the acetic acid modifier is present in an amount of from about 0.16 mole percent to about 0.34 mole percent modifier to alpha olefin.
5. The process of claim 1 wherein the temperature in the reaction zone is maintained within the range of from about 30 degrees C to about 150 degrees C.
6. The process of claim 5 wherein the temperature range is from about 40 degrees C to about 60 degrees C.

7. The process of claim 1 wherein the alpha olefin is a monounsaturated alpha olefin having from 3 to about 22 carbon atoms.
 8. The process of claim 7 wherein the alpha olefin contains from 3 to about 14 carbon atoms.
5
 9. The process of claim 8 wherein the alpha olefin is selected from the group consisting of propene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-decene, 1-dodecene, and 1-teradecene.

ABSTRACT

In process for the oligomerization of an alphaolefin, a carboxylic acid modifier,
such as acetic acid, is used to increase the amount of trimer and tetramer in
5 the product.

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COMBINED DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name;

I BELIEVE I AM THE ORIGINAL, FIRST, AND SOLE INVENTOR (if only one name is listed below) OR AN ORIGINAL, FIRST, AND JOINT INVENTOR (if more than one name is listed below) OF THE SUBJECT MATTER WHICH IS CLAIMED AND FOR WHICH A PATENT IS SOUGHT ON THE INVENTION

Entitled: OLIGOMERIZATION OF ALPHA-OLEFINS IN THE PRESENCE OF CARBOXYLIC ACIDS

the specification of which:

(check
one) is attached hereto:

was filed on as
Application Serial No.

and was amended on

(if applicable)

I HAVE REVIEWED AND UNDERSTAND THE CONTENTS OF THE ABOVE-IDENTIFIED SPECIFICATION, INCLUDING THE CLAIMS, AS AMENDED BY ANY AMENDMENT REFERRED TO ABOVE:

I ACKNOWLEDGE THE DUTY TO DISCLOSE INFORMATION WHICH IS MATERIAL TO THE PATENTABILITY OF THIS APPLICATION IN ACCORDANCE WITH TITLE 37, CODE OF FEDERAL REGULATIONS, Sec. 1.56(a) which states: "A patent by its very nature is affected with a public interest. The public interest is best served, and the most effective patent examination occurs when, at the time an application is being examined, the Office is aware of and evaluates the teachings of all information material to patentability. Each individual associated with the filing and prosecution of a patent application has a duty of candor and good faith in dealing with this Office, which includes a duty to disclose to the Office all information known to that individual to be material to patentability as defined in this section. The duty to disclose information exists with respect to each pending claim until the claim is cancelled or withdrawn from consideration, or the application becomes abandoned".

I hereby claim foreign priority benefits under Title 35, United States Code Sec. 119 and/or Sec. 365 of any foreign application(s) for patent or inventor's certificate as indicated below and have also identified below any foreign application for patent or inventor's certificate on this invention having a filing date before that of the application on which priority is claimed:

COUNTRY/INTERNATIONAL	APPLICATION NUMBER	DATE OF FILING (Day, Month, Year)	PRIORITY CLAIMED
None	None		Yes <input type="checkbox"/> No <input checked="" type="checkbox"/>

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations § 1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

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None	None	None

I HEREBY APPOINT THE FOLLOWING AS OUR ATTORNEYS WITH FULL POWER OF SUBSTITUTION TO PROSECUTE THIS APPLICATION AND TRANACT ALL BUSINESS IN THE PATENT AND TRADEMARK OFFICE CONNECTED THEREWITH:

W. Keith Turner	REGISTRATION NO.	ASSOCIATE POWER OF ATTORNEY ATTACHED
A. H. Uzzell	26,816	Yes <input type="checkbox"/> No <input checked="" type="checkbox"/>
J.W. Ambrosius	27,602	
	27,705	

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Chevron Corporation
Law Department
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San Ramon, CA 94583-0806

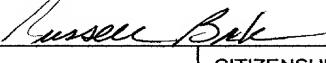
ASSOCIATE POWER OF ATTORNEY ATTACHED
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FULL NAME OF SOLE OR FIRST JOINT INVENTOR	SIGNATURE	DATE
EDUARDO J. BARALT		9-25-00

RESIDENCE	CITIZENSHIP
3603 Sweetgum Hill, Kingwood, Texas 77345	U.S.A. Venezuela

POST OFFICE ADDRESS
(Same as above)

FULL NAME OF SECOND JOINT INVENTOR, IF ANY	SIGNATURE	DATE
RUSSELL BAK		9-25-00

RESIDENCE	CITIZENSHIP
101 South Spiral Vine, The Woodlands, Texas 77381	U.S.A.

POST OFFICE ADDRESS
(Same as above)

Please see attached continuation page for additional inventors.